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THE SEPARATION OF MICROGRAM QUANTITIES OF $^{252}_{98}Cf$ AND $^{248}_{96}Cm$ BY EXTRACTION CHROMATOGRAPHY IN A HIGH-LEVEL CAVE

by

E. P. Horwitz, C. A. A. Bloomquist,

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Chemistry Division

February 1969

TABLE OF CONTENTS

LIST OF FIGURES

TABLE

THE SEPARATION OF MICROGRAM QUANTITIES OF $^{252}_{98}Cf$ AND $^{248}_{96}Cm$ BY EXTRACTION CHROMATOGRAPHY IN A HIGH-LEVEL CAVE

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ABSTRACT

The extraction chromatography technique was applied to the separation of microgram quantities of ^{248}Cm from hundred-microgram quantities of ^{252}Cf. Di(2-ethylhexyl) orthophosphoric acid adsorbed on hydrophobic Celite was used as the column material. Dilute nitric and hydrochloric acids were used as the elutriants. Column runs were performed in a high-level cave with 48-in. concrete shielding. Decontamination factors of ^{252}Cf from the ^{248}Cm of 10^8-10^9 were obtained in a single-column run.

I. INTRODUCTION

During the last few years microgram to milligram quantities of the isotope $^{252}_{98}Cf$ (alpha half-life of 2.65 yr) have become available from the Oak Ridge National Laboratory. The primary uses of this isotope have been as a neutron source, as a result of its 85-yr spontaneous-fission half-life, and as a target for the production of einsteinium by neutron irradiation. However, as larger quantities of $^{252}_{98}Cf$ become available, another important use of this isotope will be as a source of $^{248}_{96}Cm$, which is the daughter of $^{252}_{98}Cf$ and is one of the most stable isotopes of curium. Its alpha half-life (3.84×10^5 yr) and alpha specific activity (8.34×10^3 d/min/μg) (Ref. 1) are $>10^4$ times the alpha half-life and $< 10^4$ times the specific activity of the most readily available isotope of curium, namely, $^{244}_{96}Cm$. Because of its stability, $^{248}_{96}Cm$ is one of the best sources of curium for the preparation and study of the chemical compounds of this element.

This report describes an extremely rapid and efficient method for separating $^{248}_{96}Cm$ from microgram quantities of its parent, $^{252}_{98}Cf$. The separation is based on the large difference in the extractability of Cm(III) and Cf(III) by the extractant di(2-ethylhexyl) orthophosphoric acid (HDEHP). The $^{248}_{96}Cm$ and $^{252}_{98}Cf$ are separated on an extraction chromatography column containing HDEHP. Because of the large number of neutrons emitted by

microgram quantities of $^{252}_{98}Cf$, it is necessary to perform the separation by remote control in a high-level cave. A containment box within the cave houses the equipment and apparatus used for the separation.

II. EXTRACTION CHROMATOGRAPHY OF Cm(III) AND Cf(III) WITH HDEHP

The conditions for "milking" microgram quantities of $^{252}_{98}Cf$ for its daughter $^{248}_{96}Cm$ are based on extensive tracer-scale data on the extraction chromatography of Am(III), Cm(III), Bk(III), Cf(III), Es(III), and Fm(III) with HDEHP, which has been obtained by the authors[2,3] during the last few years. The column material consisted of HDEHP adsorbed on a hydrophobic diatomaceous earth support (Celite-545) (see Sect. IV). Many column parameters were evaluated in these studies; however, only the data that are pertinent to the Cm-Cf separation will be presented here. The tracer-scale Cm-Cf data, together with some data for americium and berkelium, will be published in a more complete form elsewhere.[3]

Table I shows the separation factor Cf(III)/Cm(III) at four different temperatures obtained with dilute HNO_3 and HCl elutriants. The column contained 88.2 mg HDEHP/g of dry bed. The separation factors were calculated by use of the equation

$$C = (V_{max} - v_m)/v_m, \qquad (1)$$

where V_{max} is the volume of eluate to peak maximum, v_m is the void volume or volume of the mobile phase, and C is the number of free column volumes to peak maximum.

TABLE I. Separation Factor, Cf(III)/Cm(III), for the Extraction Chromatography System HDEHP on Celite

Temp, °C	HNO_3 Elutriant	HCl Elutriant
25	26	32
45	24	28
60	22	25
75	20	23

The data in Table I show that the separation factor is relatively insensitive to temperature. In addition, the difference for HNO_3 and HCl is also very small. Since column performance (measured by calculating the plate height) was found to be substantially higher at higher temperatures for Es(III),[2] a temperature of 60°C was selected as a convenient temperature at which to carry out the separation of curium and californium.

Figure 1 shows the acid dependency of the K_d of Cm(III) and Cf(III) at 60°C. The column again contained 88.2 mg of HDEHP/g of dry bed. The values of K_d were calculated by use of the equations

$$V_{max} = v_m + K_d v_s \quad (2)$$

and

$$K_d = C(v_m/v_s), \quad (3)$$

where K_d is the distribution coefficient and v_s is the volume of stationary phase (HDEHP). The value of v_s is obtained by dividing the weight in grams of HDEHP in a column by the density of HDEHP (0.975 g/ml). By means of Eqs. 2 or 3 and the data in Fig. 1, the acidity of the elutriant required to elute curium and californium over a wide range of values of V_{max} or C can be calculated.

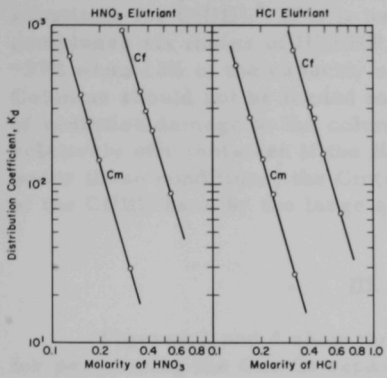

Fig. 1. Concentration of Hydrogen Ion for the Elution of Cm(III) and Cf(III) from HDEHP on Celite: 88.2 mg of HDEHP/g of Dry Bed; flowrate ≃ 1.2 ml/cm^2/min, 60°C

Figure 2 shows a typical Cm(III)-Cf(III) tracer-scale separation. The values of v_s and v_m for this particular column were 0.021 and 0.46 ml, respectively. An acid concentration (HCl in this case) was calculated to elute curium in the first free-column volume (C in the range from 0 to 1).

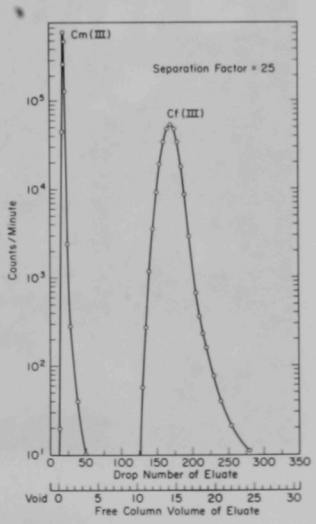

Fig. 2

The Elution of Cm(III) and Cf(III) with 0.41 N HCl from HDEHP on Celite: 88.2 mg of HDEHP/g of Dry Bed, Flowrate: 1.3 ml/cm^2/min, 60°C. Column bed size: 0.0620 cm^2 x 10 cm; bed density: 0.371 g/ml; drop volume: 39 µl/drop; f = 0.72.

In applying the extraction chromatography system to the separation of μg to mg samples of $^{252}_{98}Cf$-$^{248}_{96}Cm$, the effect of mass on the K_d must also be taken into account. The mass effect was studied using Eu(III) as a substitute for Cf(III).[3] If it is assumed that one mole of Eu(III) [or Cf(III)] complexes six moles of HDEHP, the reduction in the K_d of Eu(III) was ~37% when 12% of the capacity of the column was complexed by Eu(III). Columns should not be loaded much beyond 12% of their capacity because of radiation damage to the column. The Cm-Cf separation should still be relatively efficient even if the K_d of Cf(III) was reduced by 37%. Actually, under these conditions, the Cm(III) band would be readily displaced in front of the Cf(III) band by the large quantity of californium.

III. EQUIPMENT

Figures 3 and 4 show the general layout and apparatus employed for performing the Cm-Cf separation by remote control in a high-level cave with 48-in. concrete shielding. The equipment utilized and the materials of construction employed are listed in the Appendix. In most cases standard-size glassware and equipment were used in the containment box. However, in certain situations equipment was modified in order to permit easy handling with the master-slave manipulators.

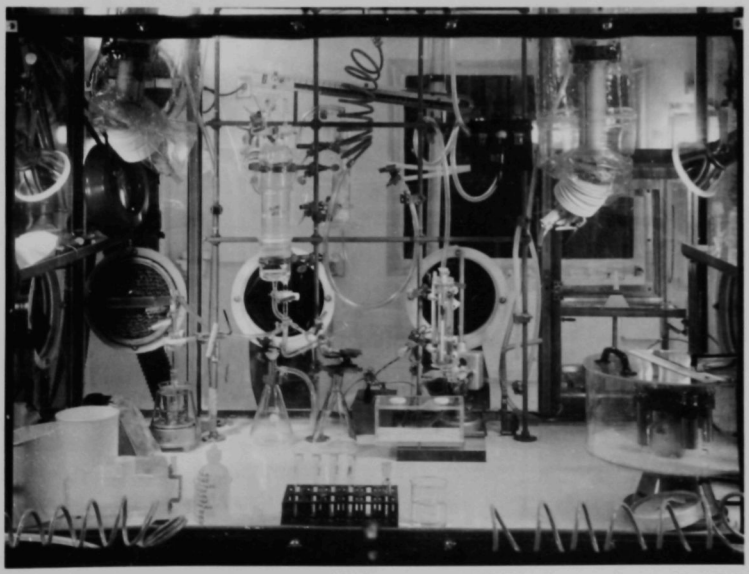

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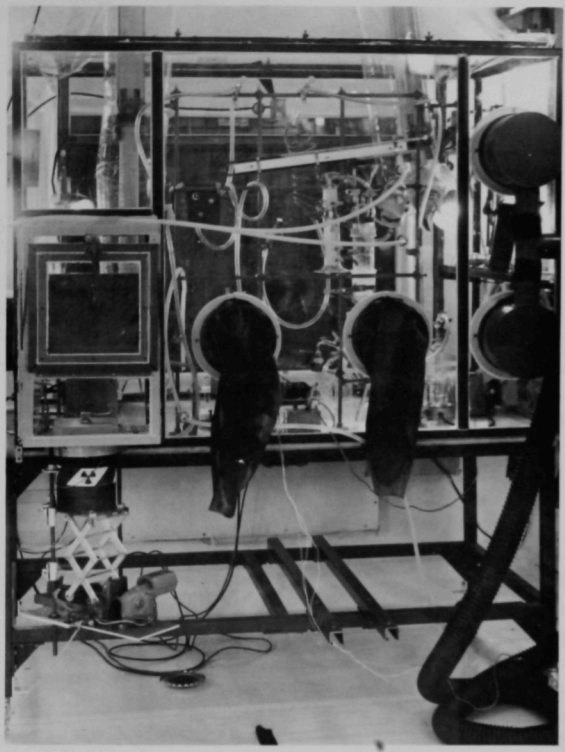
Fig. 3. Inside View of Containment Box



121-4075

Fig. 4. Back of Containment Box Showing Transfer Port and Can-out System

The equipment in the containment box was designed to reduce significantly the causes and spread of radioactive contamination. The two major causes of contamination in remote-control operations, such as those described below, are in the handling and removal of radioactive waste and in the evaporation of highly radioactive solutions. Waste removal was performed by means of a remote one-gallon waste-transfer system, shown in Fig. 4. All liquid waste was absorbed in vermiculite which was subsequently placed, along with other solid waste, in ice-cream cartons (see Fig. 3, extreme front left side of the containment box). The cartons were then placed in one-gallon cans housed in the bottom of the transfer port. The floor of the containment box was covered with Formica to facilitate the cleanup of any "spills."

Evaporations were performed by drawing air over the top of the evaporating solution and up through a tube, which was clamped ~1-2 in.

above the top of the solution. The vapors were then passed from the tube through a trap containing dilute HCl (see Fig. 3). The negative pressure in the evaporation system was maintained by means of a light-duty vacuum pump.

IV. PROCEDURE

A. Preparation of Column Material and Columns

The HDEHP used in preparing the column material was purified following the procedure of Peppard et al.[4] A commercial diatomaceous earth, Celite 545, was used as the solid support for the HDEHP. The Celite was graded by means of a grading apparatus almost identical to that described by Aly and Latimer.[5] The optimum particle-size fraction, which was found by previous studies[2] to have a settling rate of 1.0-1.3 cm/min, was selected for the preparation of the column material. The graded Celite was then made hydrophobic by exposing to the vapors of dimethyldichlorosilane (DMCS) in a vacuum system.[2]

The HDEHP-Celite column material was prepared by mixing the appropriate amounts of graded hydrophobic Celite and purified HDEHP with acetone and evaporating the excess solvent at room temperature. Two column materials of different capacity were prepared. The quantities used in preparing the small-capacity material, which contained 88.2 mg (0.27 mmol) of HDEHP/g of dry column material, were the following: 193 mg of HDEHP, 20-25 ml of acetone, and 2 g of Celite. The large-capacity material, which contained 162 mg (0.50 mmol) of HDEHP/g of dry column material, was prepared as described above except that the quantity of HDEHP was doubled.

Pyrex glass columns (of ~2.8 and 4.0 mm ID) were used for all separations. The columns were exposed a minimum of 30 min to DMCS vapors in a desiccator, then washed with acetone, air dried, and weighed. The bed volume and cross-sectional area of the columns were measured by weighing the volume of water (while in the column) between two marks 10 cm apart. After drying, the columns were filled by gently tamping the dried HDEHP-Celite material to form a bed 10 cm in length. The columns were again weighed to obtain the weight of column material. The volume of the stationary phase, v_s, was then calculated from the quantity of HDEHP on the column (in grams) and the density of HDEHP (0.975 g/ml).

All the columns used for Cm-Cf separations were thermostated at 60°C. The columns were routinely preconditioned with 10 bed volumes of preboiled 0.1 N HNO_3 or HCl at 18-20°C and at a rapid flowrate. After preconditioning, the columns were thermostated at the proper temperature. All air pockets in the bed were removed by this procedure. The void volume v_m was measured by determining the breakthrough of ^{134}Cs.

B. Chromatographic Separation

The typical column bed size used for the $^{248}_{96}Cm$ "milking" of 100-250-μg samples of $^{252}_{98}Cf$ was 0.13 cm^2 x 10 cm and contained 545 mg of column material (162 mg of HDEHP/g of dry bed). The fractional void volume was 0.70. The values of v_s and v_m were 9.1×10^{-2} and 0.91 ml, respectively. By use of Eq. 2 and the data in Fig. 1, the acidity of elutriant required to elute curium in the first 0-2 free column volumes of eluate was calculated to be 0.46 N HNO_3. The nitric acid elutriant was selected as the elutriant for use with high levels of alpha activity even though the separation factor is slightly smaller than in the HCl system. At this acidity, the value of V_{max} for californium would be ~14 free column volumes of eluate. (The value of K_d was reduced by ~10% due to the mass of the samples.)

The californium sample was evaporated to dryness in a centrifuge tube, dissolved in a minimum volume of 0.3 N HNO_3 (~0.5 ml), and loaded on the column by means of a Berkeley pipet. Several additional 0.5-ml portions of 0.3 N HNO_3 were used to rinse the centrifuge tube and were subsequently loaded on the column. The initial portion of acid used to dissolve the californium sample and the rinses were vortexed thoroughly in the sample tube and finally centrifuged. This procedure improved the efficiency of the loading operation. The efficiency of the loading was easily determined by neutron counting the centrifuge tube which contained the californium sample.

The use of 0.3 N HNO_3 for loading and rinsing insured rapid diaplacement of the curium band away from the californium band. A few minutes after loading the californium sample on the column, the intense alpha and spontaneous-fission activity of the $^{252}_{98}Cf$ produced noticeable gas pockets in the column. After loading, the elutriant was changed to 0.46 N HNO_3. The flowrate was ~1-2 $ml/cm^2/min$. Approximately 99.5% of the curium eluted from the column in the first three free column volumes of eluate. The elution was usually continued for six free column volumes before stripping the californium from the column with 1 N HNO_3. Approximately three free column volumes of 1 N HNO_3 removed ~99.9% of the californium from the column.

The californium samples were usually evaporated to dryness and loaded on a cation exchange column (Dowex 50W, X-8) with 0.1 N HCl. (The cation exchange column was ~4 mm ID by 10 cm in length.) After loading, the column was eluted with 2-3 bed volumes of 2 N HCl. The californium was then stripped from the column with ~5 bed volumes of 6-7 N HCl. The californium samples were allowed to stand in 6-7 N HCl solution until the next $^{248}_{96}Cm$ separation. The purpose of the cation cleanup column was to remove from the californium any radiolytic decomposition products of the HDEHP which might be present, e.g., H_2MEHP or H_3PO_4.

The separated $^{248}_{96}Cm$ fraction was removed from the high-level cave and further purified by extraction chromatography using HDEHP on Celite. The column size and conditions are similar to those shown in Fig. 2.

V. RESULTS AND DISCUSSION

The curium fractions (first three free column volumes) from the first HDEHP column were consistently decontaminated from $^{252}_{98}Cf$ by a factor of 10^8-10^9. Unfortunately, the $^{252}_{98}Cf$ samples were also contaminated with other californium isotopes, namely, $^{249,250,251}_{98}Cf$, which amounted to ~25% of the total californium by mass. Thus, the final curium product contained other curium isotopes. A typical curium fraction contained ~10-12 μg of curium, 96% $^{248}_{96}Cm$-4% $^{246}_{96}Cm$ by mass and 21% $^{248}_{96}Cm$-79% $^{246}_{96}Cm$ by activity.

The procedure described above was also used to separate $^{244}_{96}Cm$ from the californium samples prior to the "milking" experiments. The decontamination of $^{244}_{96}Cm$ from 100-250-μg samples of californium was $\geq 10^3$, depending on the efficiency of loading and rinsing of the reservoir. The $^{244}_{96}Cm$ content in the $^{246,248}_{96}Cm$ was maintained at $<1\%$ by activity ($<10^{-4}\%$ by mass). During the purification of the californium samples, care was taken to minimize contamination of equipment in the containment box with $^{244}_{96}Cm$. Such contamination could result in cross-contamination of $^{246,248}_{96}Cm$ samples with $^{244}_{96}Cm$.

Figure 5 shows the final purification of 10 μg of $^{246,248}_{96}Cm$ from any traces of alkali and alkaline earth metals present and from any remaining $^{252}_{98}Cf$. The final $^{246,248}_{96}Cm$ product was spectroscopically pure (>99.9%)

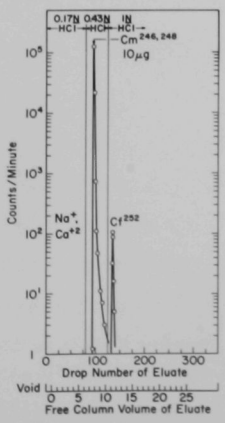


Fig. 5

The Separation of 10 µg of $^{246,248}_{96}Cm$ from $^{252}_{98}Cf$ Using HDEHP on Celite: 88.2 mg of HDEHP/g of Dry Bed, Flowrate: 1 ml/cm^2/min; 60°C. Column bed size: 0.0638 cm^2 x 10 cm; bed density: 0.412 g/ml; drop volume: 41.7 µl/drop; f = 0.72.

121-4181

from all impurities. (High-purity HCl solutions were used in the final elutions.) Thus, the extraction chromatography method with HDEHP not only decontaminated the californium from curium by many orders of magnitude ($>10^{10}$), but also gave a final product that was suitable for the preparation of curium compounds.

Although the largest quantity of $^{252}_{98}Cf$ that was "milked" for $^{248}_{96}Cm$ was 250 μg, the column size and capacity employed should handle up to 1 mg of $^{252}_{98}Cf$. Even larger samples of californium (e.g., up to 100 mg) could be "milked" in the above cave facility by increasing the column dimensions.

APPENDIX

Equipment and Materials

1. Containment Box

   a. Construction

      (1) Size: 4 ft deep, 6 ft wide, and 4 ft high
      (2) Materials
         (a) Aluminum floor plate and panels covered with No. 949 white Formica
         (b) Lucite wall sheeting
         (c) PVC corner and joining materials
         (d) Unistrut reinforcing
         (e) Plywood pallet, painted with fire-resistant paint
         (f) RTV silicone caulking
         (g) Urethane gaskets on transfer port and front panel
      (3) Boots for manipulators
         (a) Upper boot: PVC, 0.012 in. thick
         (b) Lower boot: PVC, 0.006 in. thick
         (c) Gaultlet: Hyperlon-coated urethane
      (4) Double-door transfer porch: 12- x 12- x 9-in. transfer door
      (5) Gloves on side and back of box for decontamination

   b. Ventilation for Containment Box

      (1) Inlet filters: 8-in. diameter x 6 in. thick; absolute filters (99.95% efficient)
      (2) Exhaust filters: 8-in. diameter x 6 in thick; absolute filters (99.95% efficient)
      (3) Negative pressure as per manometer = 0.250 in. of water

2. Apparatus in Containment Box

   a. Vortex mixer

   b. Self-illuminated magnifying glass

   c. Lucite tube holder for neutron counting

   d. Evaporation apparatus, in-box traps, and in-line scrubber

   e. Berkeley pipet line and glass ball-joint connector

   f. Nitrogen pressure line and glass ball-joint connector for columns

   g. Thermostated column jacket (dc coil heated) and extraction chromatography column

   h. Photoelectric-beam drop-counting device

   i. Sliding fraction collector

j. Teflon 3-way stopcock valve nitrogen pressure line selector

k. Distilled water line containment box inlet

l. Plexiglas-shielded centrifuge

m. Exit port, including upper transfer tray and lower "can-out" remote-transfer apparatus

3. External Equipment for Containment Box

a. Manipulation--Cell Interior

(1) Model 8 master-slave manipulators
(2) Extended-reach master-slave manipulators, used for transfers
(3) One-ton-capacity crane
(4) Through-wall transfer slide

b. Transport

(1) Radio-controlled "mule" for transport of sample
(2) Robot manipulator for special transfers

c. Utilities

(1) Quick-connect bulkhead and regular fittings with double-end shut-off
(a) 1/4-in. ID for gas
(b) 3/8-in. ID for liquids
(2) Self-storing coil hose for some liquids and gases
(3) Halon-1301 fire-extinguisher system[6]
(4) AC-DC variable electricity
(5) Vacuum pump, light duty, for evaporation unit
(6) Neutron detector ($^{235}_{92}U$) mounted under containment box
(7) Remote one-gallon transfer system[7]

ACKNOWLEDGMENT

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